

Table 25

Examples and Comparative Examples	Production of solvent-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 199	Example 185	Aminoalkyd resin	717
Example 200	Example 186	Aminoalkyd resin	870
Example 201	Example 187	Aminoalkyd resin	666
Example 202	Example 188	Aminoalkyd resin	538
Example 203	Example 189	Aminoalkyd resin	845
Example 204	Example 190	Aminoalkyd resin	923
Example 205	Example 191	Aminoalkyd resin	666
Example 206	Example 192	Aminoalkyd resin	589
Example 207	Example 193	Aminoalkyd resin	742
Example 208	Example 194	Aminoalkyd resin	845
Example 209	Example 195	Aminoalkyd resin	640
Example 210	Example 196	Aminoalkyd resin	717
Example 211	Example 197	Aminoalkyd resin	870
Example 212	Example 198	Aminoalkyd resin	896
Comparative Example 79	Comparative Example 76	Aminoalkyd resin	512
Comparative Example 80	Comparative Example 77	Aminoalkyd resin	840
Comparative Example 81	Comparative Example 78	Aminoalkyd resin	2,944

Table 25 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 199	100	15.7	7.3	0.8
Example 200	105	16.8	8.6	0.7
Example 201	98	16.6	7.1	0.8
Example 202	101	16.3	6.9	0.6
Example 203	91	17.8	8.1	0.8
Example 204	109	17.7	7.6	0.7
Example 205	113	17.7	7.1	0.7
Example 206	109	16.8	4.1	0.3
Example 207	108	16.8	3.6	0.3
Example 208	101	15.8	3.1	0.2
Example 209	106	16.4	2.8	0.2
Example 210	96	17.3	3.6	0.3
Example 211	131	17.1	1.3	0.3
Example 212	130	17.2	4.1	0.3
Comparative Example 79	78	22.1	11.1	1.5
Comparative Example 80	70	20.6	11.4	1.4
Comparative Example 81	43	19.4	12.8	1.3

Table 26

Examples and Comparative Examples	Production of water-based paint		Properties of paint
	Kind of black iron- based particles	Kind of resin	Viscosity (cP)
Example 213	Example 185	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 214	Example 186	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 215	Example 187	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 216	Example 188	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 217	Example 189	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 218	Example 190	Water-soluble alkyd resin Water-soluble melamine resin	923
Example 219	Example 191	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 220	Example 192	Water-soluble alkyd resin Water-soluble melamine resin	819
Example 221	Example 193	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 222	Example 194	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 223	Example 195	Water-soluble alkyd resin Water-soluble melamine resin	666
Example 224	Example 196	Water-soluble alkyd resin Water-soluble melamine resin	819
Example 225	Example 197	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 226	Example 198	Water-soluble alkyd resin Water-soluble melamine resin	845
Comparative Example 82	Comp. Ex. 76	Water-soluble alkyd resin Water-soluble melamine resin	717
Comparative Example 83	Comp. Ex. 77	Water-soluble alkyd resin Water-soluble melamine resin	896
Comparative Example 84	Comp. Ex. 78	Water-soluble alkyd resin Water-soluble melamine resin	3,584

Table 26 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 213	93	16.8	8.4	0.6
Example 214	96	17.7	7.8	0.7
Example 215	93	17.2	8.0	0.7
Example 216	98	17.6	6.8	0.8
Example 217	90	18.3	8.4	0.6
Example 218	106	17.6	8.1	0.7
Example 219	110	17.6	7.4	0.7
Example 220	100	17.8	3.8	0.3
Example 221	103	17.8	4.6	0.3
Example 222	101	17.8	4.1	0.4
Example 223	98	16.9	3.8	0.3
Example 224	96	18.5	3.2	0.2
Example 225	116	17.4	3.9	0.2
Example 226	113	17.8	3.6	0.3
Comparative Example 82	64	23.2	12.7	2.1
Comparative Example 83	60	21.6	13.6	2.1
Comparative Example 84	44	20.9	14.6	1.9

Table 27

Examples and Comparative Examples	Production of resin composition	
	Black iron-based particles	
	Kinds	Amount (part by weight)
Example 227	Example 185	5.0
Example 228	Example 186	5.0
Example 229	Example 187	5.0
Example 230	Example 188	5.0
Example 231	Example 189	5.0
Example 232	Example 190	5.0
Example 233	Example 191	5.0
Example 234	Example 192	5.0
Example 235	Example 193	5.0
Example 236	Example 194	5.0
Example 237	Example 195	5.0
Example 238	Example 196	5.0
Example 239	Example 197	5.0
Example 240	Example 198	5.0
Comparative Example 85	Comparative Example 76	5.0
Comparative Example 86	Comparative Example 77	5.0
Comparative Example 87	Comparative Example 78	5.0

Table 27 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 227	Polyvinyl chloride resin	95.0
Example 228	Polyvinyl chloride resin	95.0
Example 229	Polyvinyl chloride resin	95.0
Example 230	Polyvinyl chloride resin	95.0
Example 231	Polyvinyl chloride resin	95.0
Example 232	Polyvinyl chloride resin	95.0
Example 233	Polyvinyl chloride resin	95.0
Example 234	Polyvinyl chloride resin	95.0
Example 235	Polyvinyl chloride resin	95.0
Example 236	Polyvinyl chloride resin	95.0
Example 237	Polyvinyl chloride resin	95.0
Example 238	Polyvinyl chloride resin	95.0
Example 239	Polyvinyl chloride resin	95.0
Example 240	Polyvinyl chloride resin	95.0
Comparative Example 85	Polyvinyl chloride resin	95.0
Comparative Example 86	Polyvinyl chloride resin	95.0
Comparative Example 87	Polyvinyl chloride resin	95.0

Table 27 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 227	Calcium stearate	1.0	160
Example 228	Calcium stearate	1.0	160
Example 229	Calcium stearate	1.0	160
Example 230	Calcium stearate	1.0	160
Example 231	Calcium stearate	1.0	160
Example 232	Calcium stearate	1.0	160
Example 233	Calcium stearate	1.0	160
Example 234	Calcium stearate	1.0	160
Example 235	Calcium stearate	1.0	160
Example 236	Calcium stearate	1.0	160
Example 237	Calcium stearate	1.0	160
Example 238	Calcium stearate	1.0	160
Example 239	Calcium stearate	1.0	160
Example 240	Calcium stearate	1.0	160
Comparative Example 85	Calcium stearate	1.0	160
Comparative Example 86	Calcium stearate	1.0	160
Comparative Example 87	Calcium stearate	1.0	160

Table 27 (continued)

Examples and Comparative Examples	Properties of resin composition				
	Dispers- ing condition  (-)	Blacknes s (L* value)  (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S0) x 100 (%)		
			30 minutes	60 minutes	90 minutes
Example 227	4	17.6	0	5	5
Example 228	4	18.8	0	5	10
Example 229	5	18.6	0	5	5
Example 230	5	18.7	0	0	5
Example 231	4	19.7	0	5	10
Example 232	4	18.8	0	5	10
Example 233	4	18.7	0	5	5
Example 234	5	18.5	0	0	0
Example 235	5	18.6	0	0	0
Example 236	5	17.2	0	0	5
Example 237	5	18.3	0	0	5
Example 238	5	18.2	0	0	0
Example 239	5	18.3	0	5	5
Example 240	5	18.1	0	0	0
Comparative Example 85	3	24.4	10	15	20
Comparative Example 86	3	22.9	10	20	30
Comparative Example 87	3	21.8	10	25	35



Table 28

Examples and Comparative Examples	Kind of core particles	Production of black iron- based composite particles or black iron-based particles	
		Addition of fluoroalkylsilane	
		Additives	
		Kinds	Amount added (part by weight)
Example 245	Core particles 1	TSL-8257	2.0
Example 246	Core particles 2	TSL-8233	4.0
Example 247	Core particles 3	TSL-8262	3.0
Example 248	Core particles 4	TSL-8257	1.0
Example 249	Core particles 5	TSL-8233	10.0
Example 250	Core particles 6	TSL-8262	2.0
Example 251	Core particles 7	TSL-8257	3.0
Example 252	Core particles 8	TSL-8257	6.0
Example 253	Core particles 9	TSL-8233	4.0
Example 254	Core particles 10	TSL-8262	0.5
Example 255	Core particles 11	TSL-8257	1.5
Example 256	Core particles 12	TSL-8233	2.0
Example 257	Core particles 13	TSL-8262	0.8
Example 258	Core particles 14	TSL-8257	4.0
Comparative Example 88	Core particles 1	TSL-8257	2.0
Comparative Example 89	Core particles 3	TSL-8257	30
Comparative Example 90	Core particles 3	TSL-8257	0.005

Table 28 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of fluoroalkylsilane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 245	60	30	0.13
Example 246	60	30	0.21
Example 247	60	15	0.48
Example 248	60	20	0.07
Example 249	60	60	0.54
Example 250	30	30	0.32
Example 251	60	60	0.20
Example 252	75	30	0.40
Example 253	60	15	0.21
Example 254	60	20	0.08
Example 255	45	60	0.10
Example 256	30	30	0.11
Example 257	30	30	0.13
Example 258	60	30	0.26
Comparative Example 88	60	20	0.13
Comparative Example 89	60	30	0.2
Comparative Example 90	60	30	$3.3 \times 10^{-4}$

Table 28 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles	
	Addition of carbon black fine particles	
	Carbon black fine particles	
	Kinds	Amount added (part by weight)
Example 245	A	8.0
Example 246	A	6.0
Example 247	A	5.0
Example 248	B	13.0
Example 249	B	18.0
Example 250	C	15.0
Example 251	C	15.0
Example 252	A	10.0
Example 253	A	10.0
Example 254	A	18.0
Example 255	B	16.0
Example 256	B	9.0
Example 257	C	16.0
Example 258	C	15.0
Comparative Example 88	-	-
Comparative Example 89	A	0.01
Comparative Example 90	B	5.0

Table 28 (continued)

Examples and Comparative Examples	Production of black iron-based composite particles or black iron-based particles		
	Addition of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 245	30	60	7.42
Example 246	60	30	5.68
Example 247	45	30	4.78
Example 248	60	60	11.53
Example 249	45	75	15.16
Example 250	30	40	13.03
Example 251	45	45	13.04
Example 252	60	45	9.01
Example 253	60	60	9.09
Example 254	30	30	15.18
Example 255	30	20	13.81
Example 256	60	60	8.26
Example 257	30	20	13.76
Example 258	60	—	12.99
Comparative Example 88	-	-	-
Comparative Example 89	60	30	0.01
Comparative Example 90	60	30	4.76

Table 29

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	Average major axis diameter (average particle size) ( $\mu\text{m}$ )	Average minor axis diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation (-)
Example 245	0.32	-	-	1.47
Example 246	0.18	-	-	1.41
Example 247	0.28	-	-	1.53
Example 248	0.23	-	-	1.35
Example 249	0.40	0.051	7.8	1.53
Example 250	0.28	0.038	7.3	1.38
Example 251	0.20	0.030	6.7	1.41
Example 252	0.32	-	-	1.48
Example 253	0.19	-	-	1.41
Example 254	0.29	-	-	1.52
Example 255	0.24	-	-	1.35
Example 256	0.41	0.053	7.8	1.53
Example 257	0.29	0.040	7.3	1.38
Example 258	0.20	0.030	6.7	1.41
Comparative Example 88	0.33	-	-	1.47
Comparative Example 89	0.32	-	-	1.48
Comparative Example 90	0.28	-	-	1.51

Table 29 (continued)

Examples and Comparative Examples	Properties of black iron-based composite particles or black iron-based particles			
	BET specific surface area (m <sup>2</sup> /g)	Mn content (wt. %)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 245	5.0	12.1	16.4	7.1
Example 246	7.4	14.7	18.0	8.6
Example 247	5.3	-	17.2	6.9
Example 248	13.0	-	16.6	5.8
Example 249	21.6	-	17.7	5.9
Example 250	89.7	14.5	17.9	6.9
Example 251	46.6	11.8	17.5	7.5
Example 252	4.8	11.5	16.6	3.6
Example 253	8.9	12.9	16.9	2.8
Example 254	13.8	-	15.8	0.6
Example 255	15.8	-	16.3	1.8
Example 256	23.6	-	17.3	3.2
Example 257	83.1	14.4	17.2	4.6
Example 258	47.1	11.5	17.2	4.8
Comparative Example 88	16.6	12.0	21.3	68.3
Comparative Example 89	4.7	13.1	23.0	-
Comparative Example 90	5.6	-	21.4	-

Table 30

Examples and Comparative Examples	Production of solvent-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 259	Example 245	Aminoalkyd resin	666
Example 260	Example 246	Aminoalkyd resin	793
Example 261	Example 247	Aminoalkyd resin	614
Example 262	Example 248	Aminoalkyd resin	666
Example 263	Example 249	Aminoalkyd resin	768
Example 264	Example 250	Aminoalkyd resin	845
Example 265	Example 251	Aminoalkyd resin	896
Example 266	Example 252	Aminoalkyd resin	614
Example 267	Example 253	Aminoalkyd resin	712
Example 268	Example 254	Aminoalkyd resin	712
Example 269	Example 255	Aminoalkyd resin	538
Example 270	Example 256	Aminoalkyd resin	640
Example 271	Example 257	Aminoalkyd resin	845
Example 272	Example 258	Aminoalkyd resin	712
Comparative Example 91	Comparative Example 88	Aminoalkyd resin	538
Comparative Example 92	Comparative Example 89	Aminoalkyd resin	845
Comparative Example 93	Comparative Example 90	Aminoalkyd resin	4,096

Table 30 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 259	105	15.9	7.8	0.7
Example 260	109	16.8	9.2	0.8
Example 261	98	16.5	8.6	0.9
Example 262	106	16.3	7.4	0.6
Example 263	93	17.3	7.3	0.6
Example 264	118	17.4	6.9	0.7
Example 265	122	17.1	8.1	0.8
Example 266	110	16.5	4.1	0.3
Example 267	111	16.6	4.6	0.3
Example 268	106	15.8	2.3	0.4
Example 269	103	15.9	1.8	0.3
Example 270	94	16.9	3.4	0.2
Example 271	128	17.2	3.2	0.4
Example 272	123	17.4	3.7	0.3
Comparative Example 91	81	22.1	11.3	1.7
Comparative Example 92	73	20.7	11.6	1.8
Comparative Example 93	48	19.8	12.5	1.6



Table 31

Examples and Comparative Examples	Production of water-based paint		Properties of paint
	Kinds of black iron- based particles	Kinds of resin	Viscosity (cP)
Example 273	Example 245	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 274	Example 246	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 275	Example 247	Water-soluble alkyd resin Water-soluble melamine resin	717
Example 276	Example 248	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 277	Example 249	Water-soluble alkyd resin Water-soluble melamine resin	922
Example 278	Example 250	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 279	Example 251	Water-soluble alkyd resin Water-soluble melamine resin	794
Example 280	Example 252	Water-soluble alkyd resin Water-soluble melamine resin	973
Example 281	Example 253	Water-soluble alkyd resin Water-soluble melamine resin	640
Example 282	Example 254	Water-soluble alkyd resin Water-soluble melamine resin	870
Example 283	Example 255	Water-soluble alkyd resin Water-soluble melamine resin	768
Example 284	Example 256	Water-soluble alkyd resin Water-soluble melamine resin	845
Example 285	Example 257	Water-soluble alkyd resin Water-soluble melamine resin	896
Example 286	Example 258	Water-soluble alkyd resin Water-soluble melamine resin	666
Comparative Example 94	Comp. Ex. 88	Water-soluble alkyd resin Water-soluble melamine resin	717
Comparative Example 95	Comp. Ex. 89	Water-soluble alkyd resin Water-soluble melamine resin	922
Comparative Example 96	Comp. Ex. 90	Water-soluble alkyd resin Water-soluble melamine resin	2,560

Table 31 (continued)

Examples and Comparative Examples	Properties of coating film			
	Gloss (%)	Blackness (L* value) (-)	Acid resistance	
			$\Delta G$ (%)	$\Delta L^*$ value (-)
Example 273	92	16.6	8.6	0.7
Example 274	96	17.1	8.7	0.8
Example 275	93	17.4	8.2	0.7
Example 276	98	17.6	7.2	0.8
Example 277	90	18.3	8.3	0.7
Example 278	106	17.5	8.1	0.8
Example 279	111	17.3	7.8	0.9
Example 280	96	17.5	4.3	0.3
Example 281	99	17.3	4.0	0.3
Example 282	98	16.8	3.9	0.2
Example 283	97	17.3	2.1	0.2
Example 284	91	18.1	3.6	0.3
Example 285	113	17.5	2.8	0.4
Example 286	113	17.7	2.6	0.3
Comparative Example 94	66	23.6	14.1	2.5
Comparative Example 95	63	22.0	14.8	2.0
Comparative Example 96	46	21.0	14.6	1.9

Table 32

Examples and Comparative Examples	Production of resin composition	
	Black iron-based particles	
	Kinds	Amount (part by weight)
Example 287	Example 245	5.0
Example 288	Example 246	5.0
Example 289	Example 247	5.0
Example 290	Example 248	5.0
Example 291	Example 249	5.0
Example 292	Example 250	5.0
Example 293	Example 251	5.0
Example 294	Example 252	5.0
Example 295	Example 253	5.0
Example 296	Example 254	5.0
Example 297	Example 255	5.0
Example 298	Example 256	5.0
Example 299	Example 257	5.0
Example 300	Example 258	5.0
Comparative Example 97	Comparative Example 88	5.0
Comparative Example 98	Comparative Example 89	5.0
Comparative Example 99	Comparative Example 90	5.0

Table 32 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kinds	Amount (part by weight)
Example 287	Polyvinyl chloride resin	95.0
Example 288	Polyvinyl chloride resin	95.0
Example 289	Polyvinyl chloride resin	95.0
Example 290	Polyvinyl chloride resin	95.0
Example 291	Polyvinyl chloride resin	95.0
Example 292	Polyvinyl chloride resin	95.0
Example 293	Polyvinyl chloride resin	95.0
Example 294	Polyvinyl chloride resin	95.0
Example 295	Polyvinyl chloride resin	95.0
Example 296	Polyvinyl chloride resin	95.0
Example 297	Polyvinyl chloride resin	95.0
Example 298	Polyvinyl chloride resin	95.0
Example 299	Polyvinyl chloride resin	95.0
Example 300	Polyvinyl chloride resin	95.0
Comparative Example 97	Polyvinyl chloride resin	95.0
Comparative Example 98	Polyvinyl chloride resin	95.0
Comparative Example 99	Polyvinyl chloride resin	95.0

Table 32 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kinds	Amount (part by weight)	
Example 287	Calcium stearate	1.0	160
Example 288	Calcium stearate	1.0	160
Example 289	Calcium stearate	1.0	160
Example 290	Calcium stearate	1.0	160
Example 291	Calcium stearate	1.0	160
Example 292	Calcium stearate	1.0	160
Example 293	Calcium stearate	1.0	160
Example 294	Calcium stearate	1.0	160
Example 295	Calcium stearate	1.0	160
Example 296	Calcium stearate	1.0	160
Example 297	Calcium stearate	1.0	160
Example 298	Calcium stearate	1.0	160
Example 299	Calcium stearate	1.0	160
Example 300	Calcium stearate	1.0	160
Comparative Example 97	Calcium stearate	1.0	160
Comparative Example 98	Calcium stearate	1.0	160
Comparative Example 99	Calcium stearate	1.0	160

Table 32 (continued)

Examples and Comparative Examples	Properties of resin composition				
	Dispers- ing condition  (-)	Blackness (L* value)  (-)	Percentage of area of deteriorated and discolored portions when heated at 190°C (S/S0) x 100 (%)		
			30 minutes	60 minutes	90 minutes
Example 287	5	17.6	0	5	5
Example 288	5	18.6	0	5	10
Example 289	5	18.1	0	5	5
Example 290	4	18.8	0	0	5
Example 291	4	19.1	0	5	10
Example 292	4	18.6	0	5	10
Example 293	5	18.7	0	5	5
Example 294	5	18.3	0	0	5
Example 295	5	18.5	0	0	0
Example 296	5	17.5	0	0	5
Example 297	5	17.9	0	0	0
Example 298	5	18.4	0	0	0
Example 299	5	18.1	0	0	5
Example 300	5	18.2	0	0	0
Comparative Example 97	3	24.5	10	15	25
Comparative Example 98	3	22.9	15	20	30
Comparative Example 99	3	22.1	15	20	35

## Claims

1. Black iron-based composite particles comprising:

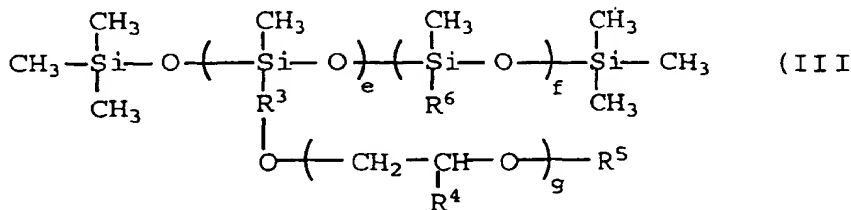
- (i) black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;  
 (ii) a coating layer on the surface of said particles, said coating layer comprising an organosilicon compound which is;

- (1) an organosilane compound obtainable by drying or heat-treating an alkoxy silane compound,  
 (2) a polysiloxane or modified polysiloxane, or  
 (3) a fluoroalkyl organosilane compound obtainable by drying or heat-treating a fluoroalkylsilane compound; and

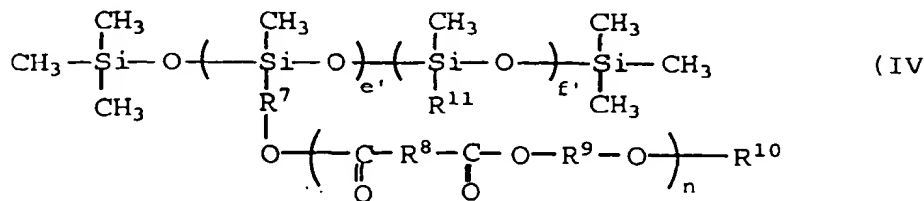
- (iii) carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered on at least a part of said coating layer,

the amount of said carbon black fine particles adhered being 1 to 30 parts by weight based on 100 parts by weight of said particles (i).

2. Composite particles according to claim 1, which further comprise an underlayer formed between said particle (i) and said coating layer (ii), comprising a hydroxide of aluminum, oxide of aluminum, hydroxide of silicon or oxide of silicon.
3. Composite particles according to claim 2, wherein the amount of said hydroxide of aluminum or silicon, or oxide of aluminum or silicon is 0.01 to 50 % by weight, calculated as Al or  $\text{SiO}_2$ , based on the weight of said black iron oxide particles or black iron oxide hydroxide particles.
4. Composite particles according to any one of the preceding claims, wherein said modified polysiloxane is  
 (A) a polysiloxane modified with a polyether, polyester or epoxy compound; or  
 (B) a polysiloxane whose molecular terminal is modified with a carboxylic acid group, alcohol group or a hydroxyl group.
5. Composite particles according to claim 4, wherein said polysiloxane (A) is of formula (III), (IV) or (V):

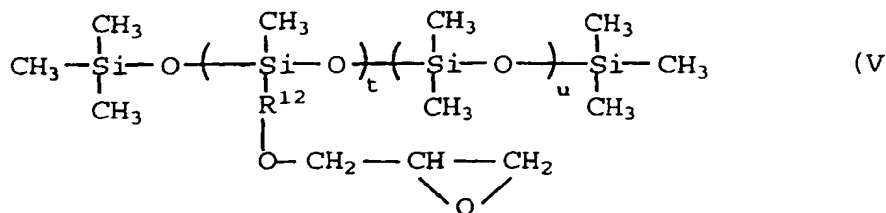


wherein  $\text{R}^3$  is  $-(\text{CH}_2)_h-$ ;  $\text{R}^4$  is  $-(\text{CH}_2)_i-\text{CH}_3$ ;  $\text{R}^5$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}(\text{CH}_3)=\text{CH}_2$  or  $-(\text{CH}_2)_j-\text{CH}_3$ ;  $\text{R}^6$  is  $-(\text{CH}_2)_k-\text{CH}_3$ ; g and h are each independently an integer of from 1 to 15; i, j and k are each independently an integer of from 0 to 15; e is an integer of from 1 to 50; and f is an integer of from 1 to 300;



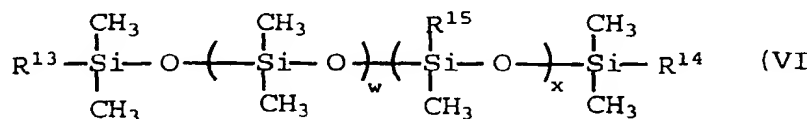
wherein  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  are each  $-(\text{CH}_2)_q-$  and may be the same or different;  $\text{R}^{10}$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}$

(CH<sub>3</sub>)=CH<sub>2</sub> or -(CH<sub>2</sub>)<sub>r</sub>-CH<sub>3</sub>; R<sup>11</sup> is -(CH<sub>2</sub>)<sub>s</sub>-CH<sub>3</sub>; n and q are each independently an integer of from 1 to 15; r and s are each independently an integer of from 0 to 15; e' is an integer of from 1 to 50; and f' is an integer of from 1 to 300; or



wherein R<sup>12</sup> is -(CH<sub>2</sub>)<sub>v</sub>-; v is an integer of from 1 to 15; t is an integer of from 1 to 50; and u is an integer of from 1 to 300.

6. Composite particles according to claim 4 or 5, wherein said polysiloxane (B) is of formula (VI):



wherein R<sup>13</sup> and R<sup>14</sup> are each -OH, R<sup>16</sup>OH or R<sup>17</sup>COOH and may be the same or different; R<sup>15</sup> is -CH<sub>3</sub> or -C<sub>6</sub>H<sub>5</sub>; R<sup>16</sup> and R<sup>17</sup> are each independently -(CH<sub>2</sub>)<sub>y</sub>-; y is an integer of from 1 to 15; w is an integer of from 1 to 200; and x is an integer of from 0 to 100.

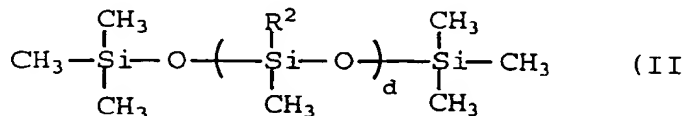
7. Composite particles according to any one of the preceding claims, wherein said alkoxy silane compound is of formula (I):



wherein R<sup>1</sup> is C<sub>6</sub>H<sub>5</sub>-, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>- or n-C<sub>m</sub>H<sub>2m+1</sub>- (wherein m is an integer of from 1 to 18); X is CH<sub>3</sub>O- or C<sub>2</sub>H<sub>5</sub>O-; and a is an integer of from 0 to 3.

8. Composite particles according to claim 7, wherein said alkoxy silane compound is methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane or decyl trimethoxysilane.

9. Composite particles according to any one of the preceding claims wherein said polysiloxane is of formula (II):



wherein R<sup>2</sup> is H- or CH<sub>3</sub>-, and d is an integer of from 15 to 450.

10. Composite particles according to claim 9, wherein said polysiloxane has methyl hydrogen siloxane units.



11. Composite particles according to any one of the preceding claims, wherein said fluoroalkyl organosilane compound is of general formula (VII):



wherein  $\text{R}^{18}$  is  $\text{CH}_3$ -,  $\text{C}_2\text{H}_5$ -,  $\text{CH}_3\text{O}$ - or  $\text{C}_2\text{H}_5\text{O}$ -; X is  $\text{CH}_3\text{O}$ - or  $\text{C}_2\text{H}_5\text{O}$ -; and z is an integer of from 0 to 15; and a' is an integer of from 0 to 3.

12. Composite particles according to any one of the preceding claims which have:

a blackness ( $L^*$  value) of 15 to 18, and/or  
a particle size of 0.082 to 1.05  $\mu\text{m}$ , and/or

a BET specific surface area value of 1 to 200  $\text{m}^2/\text{g}$ , and/or  
a geometrical standard deviation of particle sizes of 1.01 to 1.8.

13. Composite particles according to any one of the preceding claims wherein said particles (i) are magnetite particles, manganese-containing hematite particles or manganese-containing goethite particles.

14. Composite particles according to any one of the preceding claims, wherein the amount of said coating organosilicon compound (ii) is 0.02 to 5.0 % by weight, calculated as Si, based on the total weight of the organosilicon compound (ii) and said particles (i).

15. A process for producing black iron-based composite particles as claimed in any one of the preceding claims, which process comprises:

(a) mixing and stirring said particles (i) together with a silicon-containing compound which is:

- (1) an alkoxyasilane compound,
- (2) a polysiloxane or modified polysiloxane, or
- (3) a fluoroalkylsilane compound using an edge runner, thereby coating the surface of said particles (i) with said compound;

(b) adding carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$  in an amount of 1 to 30 parts by weight based on 100 parts by weight of said particles (i), thereby obtaining mixed particles; and  
(c) mixing and stirring said mixed particles using an edge runner, followed by  
(d) drying or heat-treating, thereby adhering said carbon black fine particles on the surface of a coating layer comprising the organosilicon compound.

16. A process according to claim 15, wherein said particles (i) have been coated with a hydroxide of aluminum, oxide of aluminum, hydroxide of silicon or oxide of silicon.

17. A paint comprising:

said black iron-based composite particles as claimed in any one of claims 1 to 14 or as produced by a process according to claims 15 or 16; and  
a paint base material.

18. A paint according to claim 17, wherein the amount of said composite particles is 1.0 to 100 parts by weight based on 100 parts by weight of said paint base material.

19. A rubber or resin composition comprising:

said black iron-based composite particles as claimed in any one of claims 1 to 14 or as produced by a process according to claims 15 or 16; and  
a base material for a rubber or resin composition.

20. A rubber or resin composition according to claim 19, wherein the amount of said composite particles is 0.5 to 200 parts by weight based on 100 parts by weight of said base material.

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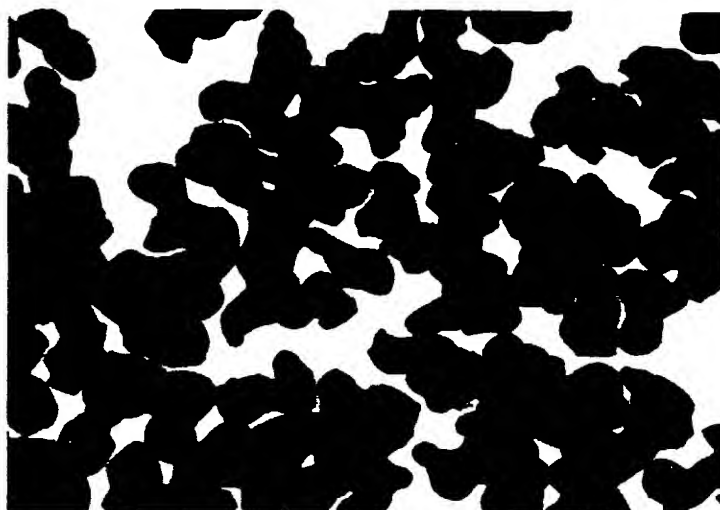
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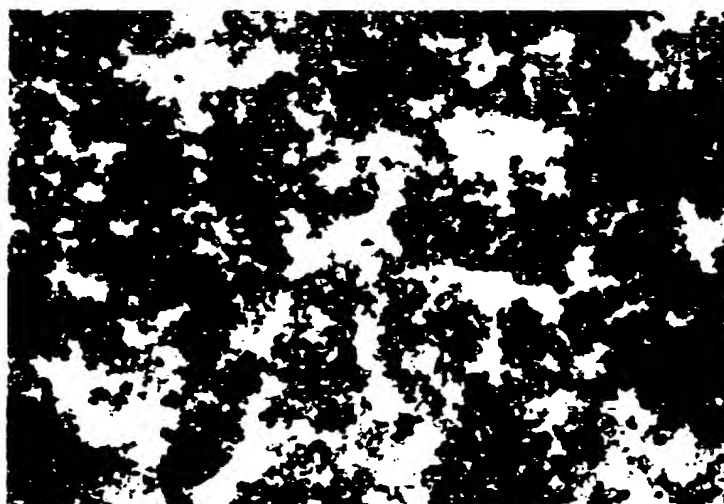
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**FIG.1**



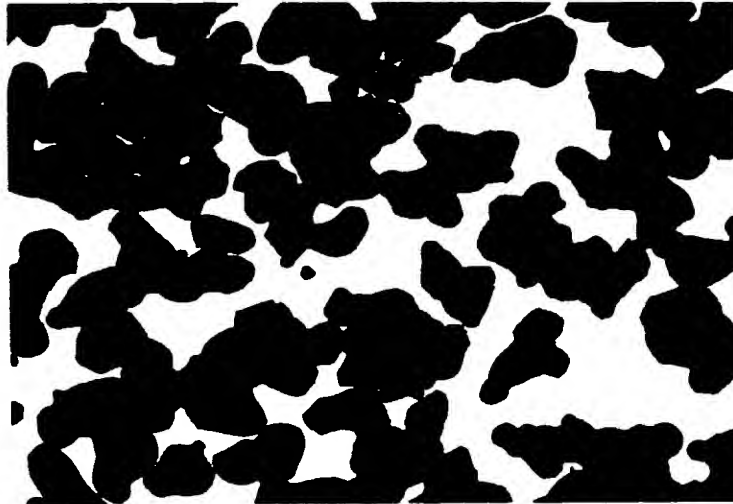
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**FIG.2**



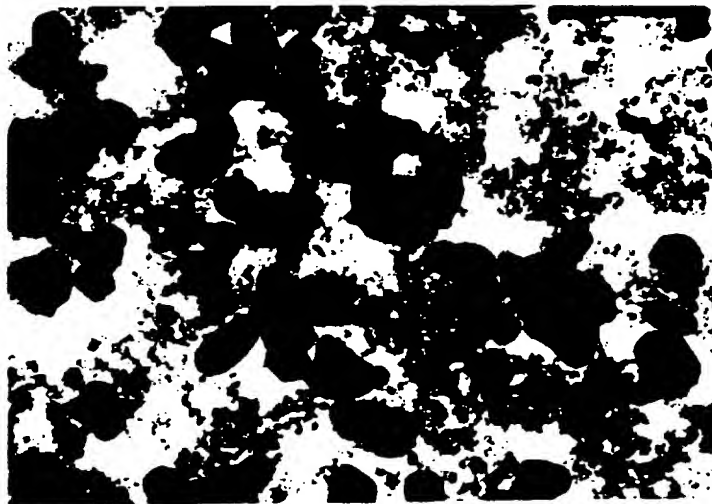
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**FIG.3**



( $\times 20000$ )

**FIG.4**



( $\times 20000$ )

(19)



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(54) **Black iron-based composite particles, process for producing the same, paint and rubber or resin composition containing the same**

(57) Black iron-based composite particles of the present invention comprise:

- (i) black iron oxide particles or black iron oxide hydroxide particles having an average particle size of 0.08 to 1.0  $\mu\text{m}$ ;
- (ii) a coating layer formed on the surface of said particles (i) said coating layer comprising an organosilicon compound which is:

- (1) an organosilane compound obtainable by drying or heat-treating an alkoxysilane compound,
- (2) a polysiloxane or modified polysiloxane, or

(3) a fluoroalkyl organosilane compound obtainable by drying or heat-treating a fluoroalkylsilane compound; and

(iii) carbon black fine particles having an average particle size of 0.005 to 0.05  $\mu\text{m}$ , adhered on at least a part of said coating layer. Such composite particles have excellent dispersibility in a vehicle, or a rubber or resin composition on the basis of a small amount of the carbon black fine particles which are desorbed from the surface of the composite particles. They also have a high blackness substantially identical to a blackness of carbon black fine particles used alone, even when carbon black is contained therein only in a small amount.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 8925

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	FR 2 030 604 A (PFIZER) 13 November 1970 (1970-11-13) * page 4, line 15-28; claims 1-14; examples 2,3 *	1, 15, 17, 19	C09C1/24 C09D5/00
A	GB 1 178 050 A (PFIZER) 14 January 1970 (1970-01-14) * claims 1-21; examples 2,3 *	1, 15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C09C C09D
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>12 August 1999</b>	Examiner <b>Drouot, M-C</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

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ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 8925

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12-08-1999

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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